

# ANALYSIS OF LIGNITE LIQUEFACTION PRODUCTS PROCESSED WITH SYNGAS AND HYDROGEN SULFIDE

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The Grand Forks Energy Technology Center has successfully processed low-rank coals in their continuous processing unit (CPU) in the bottoms recycle mode both with and without added  $H_2S$ . The addition of  $H_2S$  has been shown to enhance operability and to increase the yield and improve the quality of the distillable oils (1-3).

Products from four runs which compared the effect of added  $H_2S$  and different startup solvent were analyzed for H-donor content as a measure of recycle liquid quality and for incorporation of sulfur into organic compounds. The coal processed was a Beulah North Dakota lignite (B3).

The run conditions are shown in Table I and the coal analysis in Table II. Startup solvents included a hydrogenated anthracene oil distillate (HAODI), and surrogate recycle solvent (SS) formulated from an anthracene oil and SRC II middle distillate (4). Syngas was a 1:1 mole mixture of CO and  $H_2$ .

TABLE I  
CONTINUOUS PROCESS UNIT-SLURRY RECYCLE TEST  
RUN CONDITIONS

CPU Run No.	41	65	72	79
Start Up Solvent	HAODI	SS	SS	SS
Coal	B3	B3	B3	B3
Gas	Syngas	$H_2$	Syngas	$H_2$
Temperature, °C	460	460	460	460
Pressure, psi	4000	2600	2600	2600
Added $H_2S$	No	No	Yes	No

ANALYSIS OF BEULAH NORTH DAKOTA LIGNITE (B3)

<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>	
<u>As-received</u>		<u>Moisture-free</u>	
Moisture	28.84	Ash	16.44
Volatile matter	28.99		
Fixed carbon	30.76	<u>Moisture and ash-free</u>	
Ash	11.70	Carbon	69.49
Heating value		Hydrogen	4.43
Btu/lb	6,731	Nitrogen	0.99
		Oxygen (diff)	22.26
		Sulfur	2.81

## RESULTS AND DISCUSSION

Separations of the light oils and recycle slurry ASTM D-1160 distillates were carried out by extraction and silica gel column chromatography as described previously (5). The extraction fractions included two phenolic fractions, a basic fraction and a hydrocarbon fraction. The hydrocarbon fractions were analyzed by quantitative  $^{13}\text{C}$  NMR spectroscopy (6) and the phenols were determined by capillary gas chromatography on a 60m DB5 fused silica column (7). No significant differences in concentrations of phenols were noted, and no sulfur was detected in the phenolic fractions.

All of the extracted fractions were tested for mutagenicity (Ames test). The results showed no detectable response to the hydrocarbon and phenolic fractions from either Run 72 (with H<sub>2</sub>S) or Run 79 (without H<sub>2</sub>S). The activity of the basic fractions was within the expected response region usually associated with coal-derived liquids.

An additional separation of the light oils and recycle slurry ASTM D-1160 distillates was effected by silica gel column chromatography (5). The twelve fractions were analyzed by capillary GC (DB5 60m column) using a post-column splitter with a flame ionization detector (FID) and a flame photometric detector (FPD) specific for sulfur compounds. The concentration of the main sulfur-containing organic compound, dibenzothiophene was essentially the same for the D-1160 ASTM distillates for two of the runs (Runs 72 and 79) which were carried out with and without  $H_2S$ , 0.28 and 0.31% respectively. A typical chromatogram is shown in Figure 1. The presence of dibenzothiophene and two  $C_{11}$ -dibenzothiophene isomers was confirmed by capillary GC-MS analysis. The comparative analyses of the light oil column fractions from Runs 72 and 79, with and without  $H_2S$ , showed that the light oil from Run 72, to which  $H_2S$  was added contained a much larger variety of organic sulfur compounds and also contained elemental sulfur. Elemental sulfur elutes from the silica gel column with pentane in fractions 3 and 4 and gives an excellent response with the FPD but no response with the FID.

Analyses of the ASTM D-1160 distillate column fractions for H-donors indicated that the distillates obtained from Run 72 ( $\text{H}_2\text{S}$  added) yielded the same or higher levels of H-donors even though the partial pressure of hydrogen,  $P_{\text{H}_2}$ , was only about half that of Run 79 without  $\text{H}_2\text{S}$ . Since there is usually a strong dependence of H-donor concentrations on the  $P_{\text{H}_2}$  (Table III), this result is apparently due to the presence of  $\text{H}_2\text{S}$ .

TABLE III

COMPARISON OF H-DONOR CONCENTRATIONS AT VARIOUS  $P_{H_2}$  WITH AND WITHOUT  $H_2S$ ,  $450^\circ C$ ,  $P_T = 2600$  PSI, (% IN RECYCLE SLURRY ASTM D-1160 DISTILLATE). LIQUEFACTION OF BEULAH (B3) LIGNITE.

Run No.	65	79	72
$H_2S$	No	No	Yes
$P_{H_2}$ (psi)	2582	1986	1199
<u>H-Donors (%)</u>			
Tetralin	0.85	0.17	0.10
6-Methyltetralin	0.65	0.10	0.64
Dihydrophenanthrene	0.41	0.25	0.40
Tetrahydrophenanthrene	0.19	0.09	0.28
Octahydrophenanthrene	0	0	0.06
Dihidropyrene	0.12	0.02	0.09
Tetrahydropyrene	not determined	0.20	0.34

The presence and variety of organic sulfur compounds present in the products depends on sulfur compounds present in the starting solvent during the first 12-14 passes. Two CPU runs with B3 coal started up with different solvents showed different amounts and varieties of organic sulfur compounds in their distillable oils. Run 40 started up with AOD1 (1.4%S) gave a much more complex FPD sulfur trace for many of the silica gel column fractions than fractions from CPU runs started up with SS (0.4%S). The pattern noted is reproduced in the coal liquids formed (Figure 2).

#### CONCLUSIONS

1. A method for monitoring the presence of elemental and organic sulfur compounds in distillable low-rank coal liquefaction products utilizing column chromatography and dual detection (FID/FPD) capillary GC has been developed.
2. The addition of  $H_2S$  to the continuous processing of Beulah, North Dakota lignite does not increase the amount or variety of sulfur-containing organic compounds in the recycle slurry ASTM-D1160 vacuum distillate products. It does, however, introduce sulfur and a variety of volatile sulfur-containing organics into the light oils condensed from the vapor phase in the reactor.
3. The presence and variety of sulfur compounds after 12-14 reactor passes reflects the introduction of these components in the startup solvent.
4. No increased mutagenicity was observed with the coal liquids processed with  $H_2S$ .
5. The production of H-donors in the recycle slurry ASTM D-1160 distillates was enhanced by the presence of  $H_2S$ .

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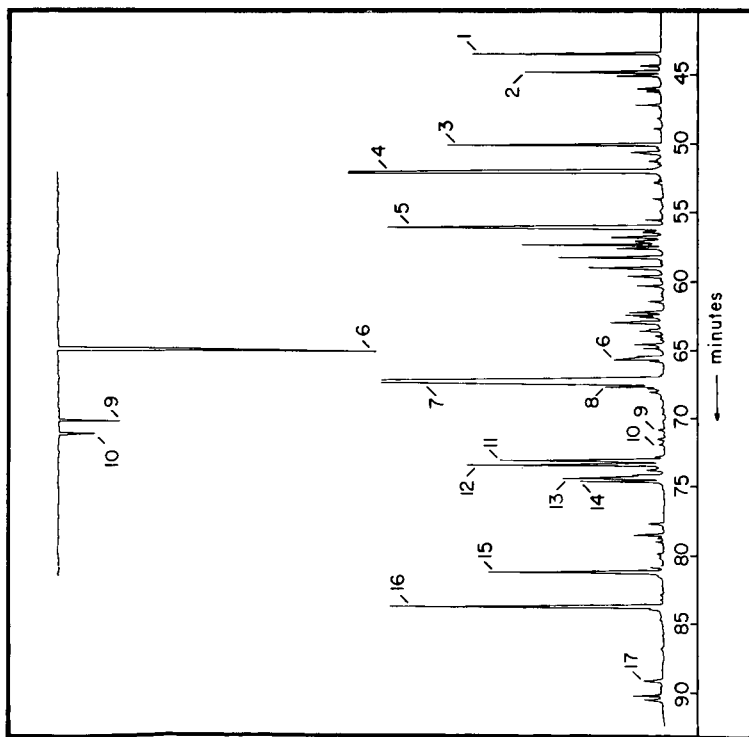


FIGURE 1. Capillary gas chromatography of light oil silica gel chromatographic fraction 7, Run 79, top trace sulfur detection by FPD, bottom trace, FID. 1. biphenyl, 2. 2-methylbiphenyl, 3. 3-methylbiphenyl, 4. dibenzofuran, 5. fluorene, 6. dibenzothiophene, 7. phenanthrene, 8. anthracene, 9. C. dibenzothiophene, 10. C. dibenzothiophene, 11. 3-methylphenanthrene, 12. 2-methylphenanthrene, 13. 4-methylphenanthrene, 14. 1-methylphenanthrene, 15. fluoranthene, 16. pyrene and 17. 2-methylpyrene

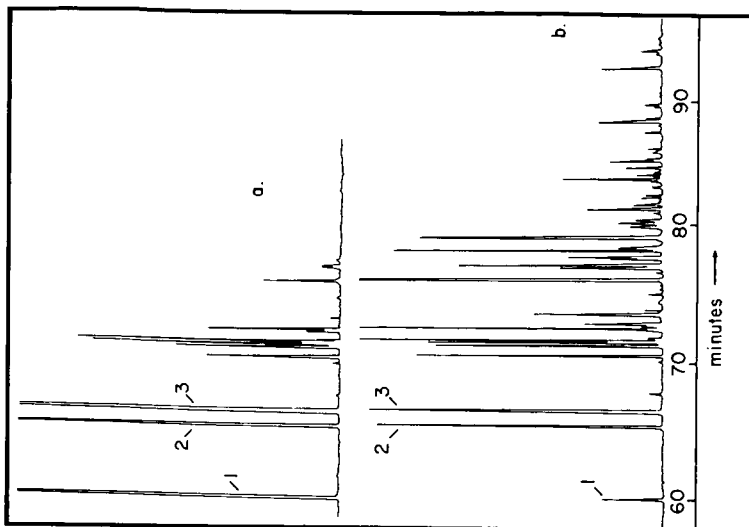


FIGURE 2. Capillary gas chromatography a). FPD trace of silica gel column fraction 7 of light oil from Run 41 b). FPD trace of silica gel column fraction 7 of anthracene oil AOD1 startup solvent. (1. dibenzothiophene, 2. Cl-dibenzothiophene and 3. Cl-dibenzothiophene).